ACTIVATION AND CLARIFYING PROPERTIES OF FULLER'S EARTH.

PART II. THE DECOLOURISING ACTION OF SOME INDIAN FULLER'S EARTHS.

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INTRODUCTION.

In the recent years, attention is centred in the various chemical factors involved in the mechanism of activation and clarifying properties of the fuller's earth. Due to the variety of the products met with, their diversity in chemical composition and due to the various factors peculiar to each process in which the earth is used, the study of its reactions has always presented great complexities, so that no generalisation which can be applied uniformly in every case has yet been possible. In Part I (This *Journal,* 1937, **20A**, 15), we have briefly dealt with the origin, nature and the common properties of the fuller's earth and also presented a summary of the different views held with regard to the mechanism of its activation and decolourising properties. The theory of physical adsorption till recently very prominently mentioned and supported by the older school, has proved to be unsatisfactory in explaining activation and decolorisation. The view that definite chemical reactions are involved in these processes is gathering increasing support and it can now be taken as established that the most important reactions involved in activation and decolorisation by fuller's earth are the base exchange reactions.

In the process of activation and decolorisation, the most important factors are the nature of the activating agent (*i.e.,* the kind of acid and its strength, etc.), the type of colouring matter to be decolourised, and the essential mineralogical constituents of the earth. The usual process of activation consists in breaking the earth with a mineral acid preferably hydrochloric acid of moderate strength. Use of too strong acid and prolonged digestion is found to effect activation adversely. In certain commercial products some residual acidity is retained by incomplete washing and is supposed to increase the activity of the earth.

Thurmann (*Ind. Eng. Chem.,* 1932, **24**, 1189) attempted to show the relationship between the pH of the clays to their decolourising efficiency. He, however, found that the addition of acid or alkali to certain clays actually decreased the decolourising power which we can now explain by the fact that only the exchangeable hydrogen of the earth is effective in decolorisation.

Colouring matter in the vegetable oils are the various plant pigments derived from the fruit and seed, usually chlorophyll, xanthophyll, or as in the case of the much-investigated cotton seed oil, gossypol and lecithin-like phosphatide, or modifications of these substances giving yellow and brown tints to the extracted oil. Their composition is largely conjectural and they occur in such small quantities that they are not easily amenable to a detailed examination. They are difficult to be extracted in pure form: colouring matter extracted from used fuller's earth does not usually possess original colour showing that its chemical nature has undergone a change. They are, however, chemically very reactive and suffer oxidation and reduction easily and also show photo-chemical activity as in the process of sun-bleaching. In the treatment of oils with fuller's earth, the acidic or basic nature of the colouring matter is of great importance. Although there is no means of directly ascertaining this acidity or basicity, it can be assumed that in most of the common oils, the colouring matter is basic in nature, as it persists even after a drastic alkaline treatment like saponification and gets easily attacked by acid earths. An activated earth therefore may not give the same quality of bleach in every oil.

The oils may also contain albuminous matter disseminated in the body of the oil in the colloidal form known as slime. The colouring matter in most cases exists independently of the slime and the two processes, *viz.*, the coagulation of the slime and the decolorisation of the oil are two distinct processes.

The essential mineralogical constituents of fuller's earth and the relative position of the various exchangeable bases in the crystal-body have been studied by various authors. According to Hofmann and co-workers (*Angew. Chem.*, 1934, 47, 539) montmorillonite ($H_2O.4SiO_2.Al_2O_3 + nH_2O$) is the essential mineral constituent of the earth while according to Longchambon (*Compt. rend.*, 1935, **201**, 483) a more general mineral resembling sapeolites in X-ray structure, but having different dehydration curves, is present in all fuller's earths. In the naturally occurring form it is a silicate of Al, Mg and Fe and forms with sapeolite and polygarskites an amorphous series of which the extreme forms are sapeolite, para-montmorillonite and nontronite. The series includes fuller's earth and smectic clays, but differs fundamentally from the kaolinic clays. It is also suggested that while clays of the first group (fuller's earths, polygarskite, etc.) are derived from the pyroxenes and amphiboles, those of kaolin are from feld spars and micas. These X-ray studies have also helped to bring out a very marked distinction between the kaolinite group of clays and the bleaching earths including fuller's earth. The kaolinitic structures are much simpler and the exchangeability of their bases is also much less. In the case of fuller's earth while Si, Al and O form the core of the crystal lattice and in the characteristic grouping preserve the basic nature and stability of the structure, the exchangeable bases, H, Ca, Mg, Fe, K, Na, either lie on its outer surface, or are easily accessible through the crystal channels. The reactivity of the earth will therefore be determined by the reactivity of these outer ions.

Folge and Olin (*Ind. Eng. Chem.*, 1933, 25, 1069) postulating the existence of *calcium zeolite* in the fuller's earth, attributed the clarifying action to the adsorptive and zeolitic action of the earth. This view cannot be correct, because the calcium content of the earth gets considerably reduced on activation and yet the earth shows increased activity.

Hofmann and co-workers (*Angew. Chem.*, 1935, 48, 187) while working with German earths have suggested that the bleaching action is effected through the chemical reaction of the *hydrogen and aluminium ions* at the surface of earths. Their results are given below:—

	Free acid in m. equivts. per 100 gms.	Quantity of the exchangeable bases in m. equivts./100 gms.			% Bleaching action in 100 gms. of oil	
		H+Al	S-value (Ca, Mg, Na, K)	T-value S+H+Al	3 gms. earth	5 gms. earth
Raw earth ..	..	4	56	60	..	32
Electrodialysed earth	..	21 23	17	61	85	90
Earth treated with 10% HCl ..	0·6	25 27	13	65	..	98
Clarit	0·6	33 28	10	71	99	100
Terrana	0·5	33 32	4	69	98	100

The bleaching action was carried with soya bean oil and the measurement of the exchangeable hydrogen ion with a solution of sodium acetate. According to these authors the process of activation is as follows: The exchangeable bases of the montmorillonite crystals get displaced by hydrogen, and alumina and ferric oxide get dissolved from the lattice of the mineral by the treatment with acids as well as by electrodialysis. Aluminium again replaces a part of the hydrogen bound to the crystalline surface. These authors have, however, overlooked the fact that aluminium being one of the most stable components of the basic silicate has much less exchangeability than even calcium or magnesium. One can therefore *prima facie* conclude that hydrogen, the content of which is increased by activation of the earth, is likely to be the most reactive element of the earths.

Indian fuller's earths have not yet been systematically studied with regard to their nature and their behaviour in activation and clarification. It was the object of the investigation here described to study the suitability of some of the Indian earths for industrial consumption in comparison with two well-known foreign earths and also to throw some light on the mechanism by which the fuller's earths effect decolorisation.

EXPERIMENTAL.

Original Earths.—The earths used in the following experiments were obtained from some of the principal deposits in India which were either in the form of fluffy powder or stratified lumps which could be easily crushed. Most of them showed high grade of purity, being free from stones, gritty matter like quartz or carbonaceous matter. The earths widely differed from each other in colour, moisture content, grain size, specific gravity, carbonate content and the amounts of colloidal matter. These are not recorded here as the experiments here described deal only with dry earths with respect to their bleaching values and zeolitic hydrogen content. None of the samples showed any evidence of organic origin (diatomecious earth) on microscopic examination and in the microphotographs (Plate I).

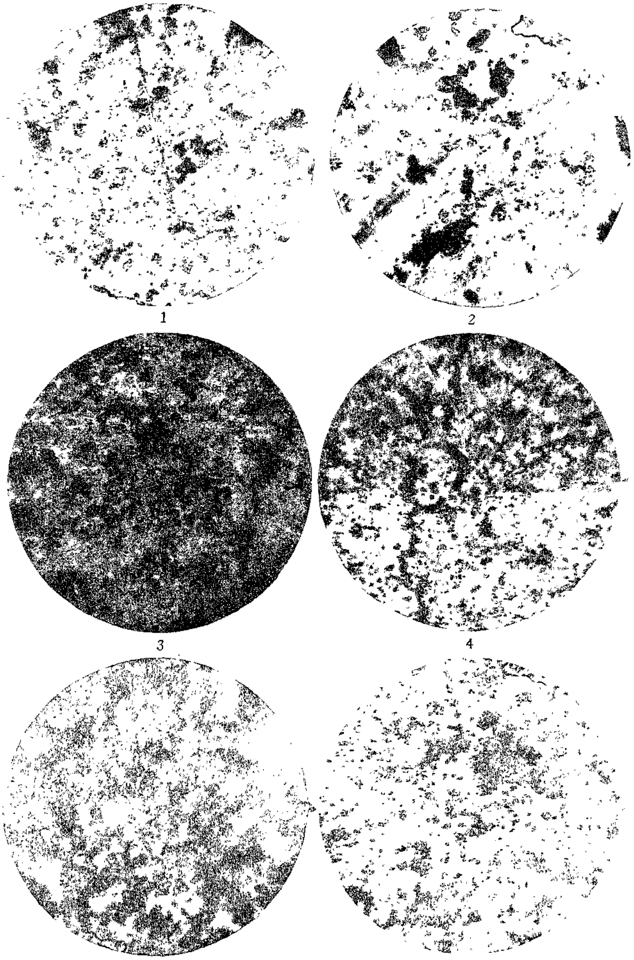
Earth	*Microscopic Appearance*
Kolhapur	Grey powder, consisting of coarse crystalline grains, with a sprinkling of black specks.
Jodhpur	Yellow grey powder, with clusters of yellow crystals with few black specks.
Bhawanagar	Light grey powder consisting of coarse grains with a higher proportion of black grains.
Murwara	Pinkish yellow powder, with yellow crystals free from black grains.

The black grains are believed to be black granite and carbonacious matter.

The original earths were dried at 90° to 95°C. and sieved uniformly through a 100 mesh-sieve and finally dried at 110°C. for about four hours.

The bleaching values of each sample were determined by agitating at 90°–95°C. a weighed quantity of earth with groundnut oil of a low acid value, the time of the duration of the agitation and the quantity of earth and oil being previously determined so as to give

PLATE I


1 2 3 4 5 6

Microphotographs of fuller's earths

1. Kolhapur
2. Jodhpur
3. Bhawanagar
4. Murwara
5. Florida
6. Germany

a widely different colour-scale in each case. The oil after agitation was filtered and the colour tints (red and yellow) were matched with a Lovibond Tintometer, with daylight as the source of light.

The relative proportions of the hydrogen-zeolite content of the earth could be determined by taking advantage of the property of exchangeability of the hydrogen with an alkaline base. This was done by shaking a quantity of earth with a solution of sodium chloride of known strength and measuring the pH of the resultant mixture with a quinhydrone electrode, after keeping the mixture overnight in a thermostat at 30°C.

The results tabulated below show the relation between the pH of the salt mixture and the change in the Lovibond units effected by the earth. The results refer to the bleach effected in a neutral groundnut oil of original colour 3.8 yellow and 0.3 red, and the pH of the mixture of 1 gram of the earth shaken with 100 cc. of 1% sodium chloride solution. The bleach in red colour, being insufficient for distinguishing purposes, was ignored. Two foreign samples of earth, one from Florida and the other from Germany (supplied by the Vereinigte Bleicherde fabriken A. G. München) were also included for comparison.

TABLE I.

Original Earths.

No.	Source	Change Lovibond units	pH	pH × Change
1	Kolhapur	1·4	7·22	10·1
2	Jodhpur	2·4	7·82	(18·7)
3	Bhawanagar ..	1·1	8·81	9·7
4	Murwara, C.P. ..	1·4	7·48	10·4
5	Florida	3·3	3·74	11·2
6	Germany	3·2	3·50	11·2
			(average)	10·5

The above results reveal clearly an inverse proportionality between the colour removed and the pH as shown by the product pH × change in Lovibond units. The proportionality cannot be strict as the pH is affected by the free alkalies contained in the earth and also by the extraneous matter like free carbonates, ferric oxide and alumina, which increase the bulk of the earth without impairing its bleaching value. Jodhpur earth was found to have high content of free alkali and the Bhawanagar earth a high content of free carbonate. The two foreign earths possess superior decolourising value compared to that of the Indian earth, and appear to be activated products.

Activated Earths.—For activation the method as given by Burgharat (*Ind. Eng. Chem.*, 1931, 23, 801) was followed:—A weighed quantity of washed earth was treated with hydrochloric acid of 19–20 Bé (added as about 20 gm. of dry HCl per 100 gm. of the earth) under reflux for three hours, washed with distilled water, the colloidal portion removed by suspension for about one hour and subsequent decantation, dried at 110°C. and weighed. Percent loss of weight on activation was also recorded.

The following table shows the relation between the bleaching value and the pH.

TABLE II.

Activated Earths.

No.	Source	% loss on activation	Change	pH	pH × Change
1	Kolhapur	10	2·9	3·76	10·9
2	Jodhpur ..	16	2·9	3·47	10·1
3	Bhawanagar..	24	3·0	4·10	12·3
4	Murwara ..	22·4	1·3	4·71	(6·1)
5	Florida ..	8	3·1	3·24	10·4
6	Germany ..	7·6	3·3	3·45	11·3
				(average)	11·0

The earths on activation give much lower pH and higher bleaching power and the inverse proportionality between the two becomes more evident.

Dehydration of the activated earths at 400°C.—In order to study the dehydration of the earths at 400°C. at which temperature they are believed to lose the maximum amount of the water of constitution, a weighed portion of each of the earth was heated to 400°C. in a muffle furnace for about two hours and the percent loss in weight, its bleaching power and pH again measured. The following results were obtained (Table III).

TABLE III.

Earth	% loss on heating at 400°C.	Change in Lovibond	pH	pH × Lovibond change
Kolhapur ..	0·89	2·0	4·95	9·9
Jodhpur ..	4·28	3·2	3·91	12·5
Bhawanagar ..	1·76	3·2	4·70	(15·0)
Murwara, C.P. ..	2·42	2·1	6·36	13·4
Florida ..	1·84	3·1	4·02	12·4
Germany ..	7·8	3·3	3·60	11·88
			(average)	12·0

The loss in weight on heating is greater in case of these earths which showed greater activity in Table II, showing thus a high content of the water of constitution and zeolitic hydrogen. On heating there is, therefore, corresponding deterioration of bleaching value with an increase of pH.

Discussion of the results.—The foregoing results bring out the close correspondence between the bleaching value of the earth and its hydrogen zeolite content, as shown by the inverse proportionality between the change in the Lovibond units and the pH of the salt-mixture. In all the different treatments to which the earths were subjected the above relationship has persisted. Another proportionality between the percent loss in weight on activation of the original earth and the corresponding pH values, as tabulated in Tables I and II, is also significant, showing that those earths having less hydrogen content, suffered greater loss on activation. Further, activation has considerably increased both hydrogen zeolite content and their bleaching power, and the inverse proportionality between the two has been much improved (pH × Lovibond change, Table II). On heating the earths to 400°C. there is deterioration in the hydrogen zeolite content with corresponding deterioration in the bleaching powers.

The Lovibond numbers are related to the transmission of light by the relation $\log T_\lambda = KN + b$ where T_λ = the transmission at a given wave-length λ, N = the Lovibond number of a given series, K and b are constants. Thus the change in Lovibond numbers is proportional to the difference of the logarithms of the reciprocal of the concentration of the colouring matter. Thus the striking proportionality observed in our experiments shows that the colour removed is directly proportional to the amount of the zeolitic hydrogen in the earths.

Our results are capable of improvement as the accuracy of the colour measurements with Lovibond Tintometer is low as compared to those of the pH measurement. The pH measurement of the salt-mixture in the manner described, however, forms a simple and easy method of ascertaining the quality of the earth for the purpose of decolorisation. Further experiments with earths activated by other methods and on the decolorisation of other vegetable oils will be described in Part III.

SUMMARY.

Indian fuller's earths have been examined with regard to their bleaching properties and the hydrogen zeolite content, and compared with two well-known foreign earths.

It has been shown that the hydrogen zeolite content of the earths is mainly responsible for decolorisation.

Dehydration of the earths at 400°C. reduces zeolitic hydrogen and the decolourising power.

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